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Description

IMPROVED PROCESS FOR PRODUCING ETHANOL

BACKGROUND OF INVENTION

[0001] Field of the Invention. This invention relates in general to processes for producing ethanol, and more particularly to methods of producing ethanol from corn.

[0002] Prior Art. With the ever-increasing depletion of economically recoverable petroleum reserves, as well as the environmental impact of the drilling processes to effect the recovery, the production of ethanol from vegetative sources as a partial or complete replacement for conventional fossil-based liquid fuels has become more attractive. A variety of vegetative materials have been utilized as the feedstock in ethanol producing processes. These would include cellulose-containing material such as scrap paper, wood or paper chips. Also various vegetable sources such as sugar beets and artichokes have been used. In addition cereal grains, such as barley and wheat

have been used as the feedstock in an ethanol producing process. However, one of the most common feedstock is whole corn kernels.

[0003] In a typical ethanol producing process it is common for these feedstock materials to first be cleaned of any foreign matter. In the case of certain cereal grains that have hulls that are not removed during the cleaning process, such as barley, it is common for the hulls of these grains to be separated from the remainder of the kernel. This would include the bran, the germ, and the endosperm. The bran is a source of nutraceutical compounds; the germ a source of oils, and the endosperm a source of starch bound in a gluten matrix that will be converted to ethanol.

[0004] In order to enhance the efficiency of converting the endosperm to ethanol it is common to mill the cleaned, and in some cases, de-hulled feedstock. The milling reduces the particle size of the kernel and breaks up any outer protective coating, such as the pericarp in a corn kernel, to expose the inner starch and protein containing components of the kernel, such as the endosperm and germ found in a corn kernel. That permits more efficient treatment by the subsequent hydrolysis and fermentation

steps. The two common milling processes are known as dry milling and wet milling. However, during dry milling too much of the starch material is lost when separating the bran and germ from the endosperm. Thus, although dry milling is substantially less capital intensive than wet milling, its use to obtain the oils or nutraceutical compounds from the germ and bran is not economically feasible. In conventional wet milling processes the oils can be separated through the use of hexane extraction. However, the hexane extraction process is slow and requires energy intensive steps to separate the oil. To economically recover the oil requires very large and expensive facilities. It would be a significant advantage to the art to provide an ethanol production process that could recover the oil and/or nutraceutical compounds in a dry mill process.

[0005] After the pretreatment steps the milled kernel particles are hydrolyzed to provide fermentable sugars. This reaction is also referred to as saccharification. Two of the most common methods of saccharification are enzymatic hydrolysis and acid hydrolysis. The sugars produced are then converted to ethanol, such as by a yeast fermentation process. A by-product of this process is an oil-containing material that can be used as animal feed. If de-

sired, a portion or all of the oil in the material can be removed and separately marketed.

[0006] Most research to date has focused on improvements to the de-braning (de-hulling for certain grains), milling, saccharification and fermentation steps in the ethanol producing process. Although progress has been made toward producing ethanol from various vegetative material, the costs of producing the ethanol and other resultant by-products has remained relative high when compared to the fossil fuel sources. Improvements to the ethanol producing process that can either achieve processing cost savings or enhanced value by-products are highly desirable.

Summary of Invention

[0007] Therefore, one object of this invention is to provide an improved ethanol producing process that provides processing cost savings and enhanced value by-products.

[0008] Another object of this invention is to provide an improved ethanol producing process that results in a more efficient milling of the feedstock.

[0009] Another object of this invention is to provide an improved ethanol producing process that results in the recovery of oils having enhanced value.

[0010] Another object of this invention is to provide an improved ethanol producing process that permits both the recovery of oils and nutraceutrical products and the use of dry milling of the feedstock.

[0011] Still another object of this invention is to provide an improved ethanol producing process that results in reduced downtime of the processing equipment.

[0012] Still another object of this invention is to provide an improved ethanol producing process that increases the through put capacity of a given ethanol producing plant.

[0013] Still another object of this invention is to provide an improved ethanol producing process that results in the recovery of an increased protein content fiber usable for animal feed.

[0014] Other objects and advantages of this invention shall become apparent from the ensuing descriptions of the invention.

[0015] Accordingly, a process for producing ethanol from vegetative material, preferably cereal grains, and more preferably corn, is provided wherein the vegetative material is first subjected to a cold solvent extraction process to remove certain nutraceutical and triglyceride oils from the vegetative material prior to the hydrolyzing treatment.

The process solvent will be selected from C_3 and C_4 hydrocarbon solvent, preferably propane. The extraction process will take place at a pressure of about 200 psig or less, and at a temperature at about 140°F. or less, for a period of time to remove the desired amount of oil from the vegetative source.

[0016] In a preferred embodiment the vegetative material will be milled whole corn kernels. In a more preferred embodiment the vegetative material will be milled to achieve a median diameter particle of about one-quarter inch or less, most preferably about seven sixty-fourth to one-quarter inch.

[0017] In another alternate embodiment utilizing corn kernels as the feedstock, the bran is separated from the germ and endosperm. The separated bran is then treated by a cold solvent extraction process to recover the valuable nutraceutical oils concentrated in the endosperm. Alternately, the germ is separated from the bran and endosperm, and the separated germ is treated by a cold solvent extraction process to recover the valuable triglycerides or other oils. Preferably, both the bran and germ are separated and treated by a cold solvent extraction process to recover the valuable nutraceutical oils and the

triglyercides.

[0018] In an alternate embodiment the vegetative material will be a grain, such as barley or wheat. In this embodiment the hulls are first removed from the grain and are subjected to a cold solvent extraction treatment to remove various oils. The de-oiled hulls are then utilized as one of the sources of the feedstock.

BRIEF DESCRIPTION OF DRAWINGS

[0019] The accompanying drawings illustrate a preferred embodiment of this invention. However, it is to be understood that this embodiment is not intended to be either exhaustive, or limiting of the invention. They are but examples of some of the forms in which the invention may be practiced.

[0020] Figure 1 is a schematic illustrating a typical prior art ethanol producing process utilizing whole corn kernels.

[0021] Figure 2 is a schematic illustrating the process steps in a preferred embodiment of the ethanol producing process of this invention wherein the milled corn kernel is subjected to a cold solvent extraction treatment prior to an acid or enzymatic hydrolysis treatment, as well as illustrating multiple preferred embodiments wherein cold solvent extraction can be used to selectively separate value-

added oil streams.

Detailed Description

[0022] Without any intent to limit the scope of this invention, reference is made to the figures in describing the preferred embodiments of the invention. The preferred embodiments of the process are described utilizing whole corn kernels as a source of the feedstock. However, cereal grains and other types of vegetative matter could be used. When cereal grains are utilized it is preferable that they first be treated to remove and separate their hulls from the remaining starch and oil containing material.

[0023] Figure 1 illustrates a typical ethanol producing process utilizing whole corn as the initial feedstock. The whole corn kernels are first cleaned in washing apparatus *1* and then subjected to either a wet milling assembly *2* or alternatively a dry milling assembly *2a*. If a wet milling process is utilized the separated germ may undergo a hexane extraction step to recover the triglycerides from the germ. The endosperm is then introduced into a hydrolysis vessel *3* where it is either enzymatically or acidly treated to convert the starch in the milled kernels into fermentable sugar compounds. If a dry milling process is used the milled kernels are then introduced into hydrolysis vessel

. The fermentable sugar compound containing stream is transferred to a fermentation vessel *4* where yeast that has been added to fermentation vessel *4* reacts with the fermentable sugar compounds to produce ethanol. By-product streams from this reaction include carbon dioxide and a substantially non-starch containing material that can be used as animal feed.

[0024] These known ethanol producing processes have several economic and efficiency draw backs. Because the corn kernel contains oils, there is an increased chance that in the dry milling operation the milling will result not in particles, but the formation of a paste-like material. The starch in the paste-like material is more difficult to chemically break down into fermentable sugar compounds during the hydrolysis step. Additionally, oil that is released from the corn kernels during the milling process remains within the milling equipment where it can becomes rancid. When this occurs, the milling process must be shut down and the equipment cleaned. An additional problem occurs when trying to separate the corn oil from the protein-containing fiber material. The oil tends to clog the filters conventionally used resulting in less efficient oil recovery. Unfortunately, the by-products obtained from the con-

ventional ethanol producing processes do not have sufficient economic value because of their relative low nutrient content to permit these processes from economically competing with conventional fossil fuel processes. These systems are further disadvantaged because of the energy cost associated with the production of the ethanol.

[0025] Referring now to Figure 2 improved alternate ethanol producing processes are disclosed that reduces or overcomes the problems associated with prior art ethanol producing processes. Again the first step is to clean the feedstock of extraneous foreign material such as dirt. If the feedstock includes hulled vegetative matter, such as cereal grains, the cleaned feedstock is first introduced in a conventional de-hulling vessel *5* where the hull are separated from the remainder of the feedstock material. However, depending on the physical and chemical composition of the hulls, it may be desirable before the de-hulling step to subject the feedstock to the cold solvent extraction process described herein to remove various pharmaceutical or neutraceutical compounds. It may also be desirable to first mill the hulls to reduce the particle size and increase the particle surface area. This reduction in particle size will in most cases permit better penetration of the solvent into the particles,

as well as obtain a more efficient extraction of the desired compounds. In general, it is desirable to subject the feed-stock as soon as possible to cold solvent extraction to begin the removal of oils from the feedstock.

[0026] In the case of vegetative matter that has no hull, such as whole corn kernels, the vegetative matter can be first treated by the cold extraction process to remove desired nutraceutical compounds found in the outer bran layer. However, it is preferred to first de-bran the whole corn kernels in a conventional de-braning assembly *6* to separate the bran and germ from the endosperm. Then one can separately treat the bran and germ and endosperm. The bran and germ, separately or together, are subjected to a cold solvent extraction process while the endosperm is fed to a conventional mill *7*, preferably a dry mill. There the endosperm and other starch containing material is reduced to particles having a median diameter of about one-quarter inch or less, preferably between about seven sixty-fourth inches to one-quarter inch. The primary oil-containing and nutraceutrical compound components (generally the germ and bran), are treated in a conventional cold solvent extraction vessel *8*. Triglycerides, as well as various other value-added oils useful in pharma-

ceutical or nutraceutical-type products are extracted from the oil-containing component in vessel *8* and recovered separately from the remaining starch and fiberous material. If desired the cold solvent extraction process can be controlled to remove only a portion of the oils. This could be desirable if there is a need for foam control in the subsequent hydrolyzing or fermentation steps. This might also be desirable if a certain level of oil is required in the fiber by-product from the fermentation step that is typically sold for animal feed.

[0027] The oil soluble fraction stream recovered from vessel *8* is introduced in a conventional solvent separator *9* whereby the solvent can be recovered and recycled to the cold solvent extraction vessel *8*. This solvent recovery step reduces costs by recycling the solvent, reduces negative environmental impact by eliminating the venting of the propane to the atmosphere, improves safety by maintaining control of the propane throughout the extraction process, and improves the quality and value of the oil by-products by removing undesired impurities. These oils form valuable by-product streams heretofore unrealized in an ethanol producing process. Preferably, the de-oiled fiber substrate recovered from vessel *8* is also introduced

in a conventional solvent separator *9a* to recover the solvent for recycling to vessel *7*. The de-oiled fiber is then transferred to a hydrolysis vessel *10* where it, along with the starch containing material from separator *7*, is subjected to hydrolysis to produce fermentable sugar-containing compounds. The hydrolysis process utilized can be any of the many known enzyme or acid treatment hydrolysis processes. These sugar-containing compounds are then subjected to fermentation in fermentation vessel *11* to produce the desired ethanol, carbon dioxide and a protein-containing fiber by-product that can be sold as animal feed. The fiber by-product can alternatively be de-oiled, again either by conventional filter units *12* or by a cold solvent extraction process. Because the bulk of the oil has been previously removed, there is less likelihood that filters would be clogged if a filter system were used. The de-oiled fiber can be used as animal feed and the extracted oil can be sold as separate valuable by-products.

[0028] *The Cold Solvent Extraction Process*The solvent extraction steps in this invention can be carried out utilizing most known solvent extraction processes; however, the use of a cold solvent extraction process is preferred. A conventional cold solvent extraction is carried out using a C_3 or C_4

hydrocarbon solvent, preferably propane, that is added to the vessel *8* after all air has been removed and the feedstock introduced. During extraction the pressure in vessel *8* is maintained at about 200 psig or less, preferable 100-140 psig, while the temperature is maintained at about 140°F or less, preferably 60°-130°F, and most preferably at 70°-110°F. As a result of the low temperatures used, proteins in the starch containing material are not denatured, as would be the case in other solvent extraction processes. In another preferred embodiment the feedstock should be introduced with as little water as possible to prevent freezing during the oil extraction stage. For this reason it is preferred that a dry milling process be used to produce the particles that will be subjected to the cold solvent extraction process. Examples of conventional cold solvent processes can be found in U.S. Patent 5,281,732 and U.S. Patent 5,707,673. The preferred solvent extraction temperature and pressure conditions will be dependent on the feedstock and the compounds that one desires to separate and recover from the feedstock.

[0029] *Alternate Pre-Treatment Processes Utilizing the Cold Solvent Process*Referring again to Figure 2, various alternate pro-

cesses for pre-treatment of the de-hulled ethanol producing feedstock is disclosed. These alternate processes can be used in lieu of or in conjunction with the cold solvent extraction step described above. In a first alternate embodiment the cleaned, de-hulled feedstock containing both the starch-containing material and oil-containing material is subjected to the cold solvent extraction process. The feedstock is introduced into extraction vessel *13* along with the solvent under extraction condition to produce an oil soluble fraction and a starch rich stream. The particular extraction conditions utilized is determined by the feedstock, the degree of extraction desired, as well as the specific compounds that one desires to extract. In a preferred embodiment the separated oil rich stream is transferred to solvent separator *14* to remove the solvent from the stream. The recovered solvent is then recycled to vessel *13*. The oil rich stream can then be separately recovered and sold as a value-added by-product of the ethanol production process. The remaining starch rich stream is then introduced into dry mill *7* for milling into smaller particles. There are several advantages of this embodiment. First, the non-ethanol producing fraction of the feedstock is separated in the first stages of the process.

This increases the production capacity of the existing ethanol producing plant facility. In addition the removal of the oil from the feedstock entering the dry mill *7* reduces or eliminates many of the prior art problems discussed above that are associated with current milling operations.

[0030] In a second alternate embodiment, the milled feedstock is subjected to a cold solvent extraction. This extraction can be in lieu of or as a supplement to the pre-milling extraction. Similarly as before the milled feedstock is introduced into extraction vessel *15* along with the solvent under extraction condition to produce an oil soluble fraction and a starch rich stream. The particular extraction conditions utilized is determined by the feedstock, the degree of extraction desired, as well as the specific compounds that one desires to extract. In a preferred embodiment the separated oil rich stream is transferred to a solvent separator *16* to remove the solvent from the stream. The recovered solvent is then recycled to vessel *15*. The oil rich stream can then be separately recovered and sold as a value-added by-product of the ethanol production process. The remaining starch containing stream is then introduced into separation vessel *7* to remove additional oil containing material, or transferred to hydrolysis vessel *10*.

[0031] It is noted that the bran layers from cereal grains contain oils that have pharmaceutical uses. Thus, if a cereal grain is used as the feedstock, it is preferred to first de-hull the grain and subject the bran layers, preferably ground, to a cold solvent extraction process to recover these pharmaceutical oils. As such, the oil from the bran has potential economic value as a by-product of the ethanol producing process. The extraction can be performed on the bran separate from the other components of the grain or they can be combined with the de-hulled, milled grain particles for introduction into cold solvent extraction vessel *8*.

[0032] In an another alternate process the starch-containing material from extraction vessel *8* can be transferred to a conventional protein extraction unit *17* to separate a recoverable valuable protein-rich stream from the starch-containing material prior to hydrolysis.

[0033] In addition to producing several value added oil by-products and the improved milling process discussed above, the removal of the oil prior to the hydrolysis treatment results in a feedstock that is higher in protein and starch content. This permits the processing of more ethanol producing starch with the same equipment that is already being used, as well as resulting in a higher protein

content animal feed by-product. Additionally, because of the improved feedstock that is utilized in the hydrolysis step there is increased cost efficiency due to the use of less heat per gallon of ethanol produced. These energy savings result at least in part from removing a substantial portion of the oil prior to the hydrolysis step.

[0034] Although the preferred embodiments have been described indicating use of multiple extraction and solvent separator vessels, it is within the scope of this invention that one or more of the extraction processes could utilize the same extraction and/or solvent separator vessels. There are of course other alternate embodiments that are obvious from the foregoing descriptions of the invention which are intended to be included within the scope of the invention as defined by the following claims.